Chapter 4
PCBs/trans-Nonachlor in Tributaries

4.1 Results

A total of 354 samples were collected from 11 tributaries that flow into Lake Michigan or Green Bay and analyzed for PCBs and *trans*-nonachlor. The samples were collected as described in Section 2.5.2, by pumping 80 to 160 L of river water through a cartridge packed with 250 g of XAD-2®, a macroreticular resin that traps hydrophobic organic contaminants. A "pentaplate" filter was installed in the sampling train front of the XAD-2® cartridge to collect the particulate matter suspended in the sample. Separate analyses were performed on the XAD-2® resin and the filtered particulates from each sampling effort, yielding results for operationally defined "dissolved" and "particulate" PCBs (Table 4-1) and *trans*-nonachlor (Table 4-2). Interferences and laboratory accidents reduced the number of *trans*-nonachlor results to 338 dissolved results and 350 particulate results.

As noted in Chapter 2, there are 209 possible PCB congeners, and the investigators in this study reported results for 65 to 110 of these congeners, depending on the capabilities of each laboratory. From March 1994 through October 1994, the analyses performed at the University of Wisconsin, Wisconsin State Lab of Hygiene determined results for 65 congeners or co-eluting congeners. In November 1994, the laboratory instituted a change in their standard operating procedure that allowed them to report the results for 78 congeners or coeluting congeners. For the purposes of this report, we are presenting summaries of the results for the following subset of all of the analytes:

- PCB congener 33
- PCB congener 118
- PCB congener 180
- Total PCBs
- *trans*-nonachlor

Table 4-1. Number of Tributary Samples Analyzed for Dissolved and Particulate PCB Congeners and Total PCBs

Tributary	Sampling Dates	Dissolved PCBs	Particulate PCBs	Total Samples
Fox River	04/07/94 to 10/12/95	39	39	78
Grand Calumet	08/04/94 to 10/18/95	15	15	30
Grand River	04/11/94 to 10/31/95	47	47	94
Kalamazoo	04/12/94 to 10/30/95	38	38	76
Manistique	04/11/94 to 10/26/95	28	28	56
Menominee	04/13/94 to 10/11/95	24	24	48
Milwaukee	03/29/94 to 10/06/95	38	38	76
Muskegon	04/14/94 to 12/05/95	28	28	56
Pere Marquette	04/05/94 to 10/18/95	28	28	56
Sheboygan	04/06/94 to 10/24/95	36	36	72
St. Joseph	04/06/94 to 10/27/95	33	33	66
	Total	354	354	708

Table 4-2. Number of Tributary Samples Analyzed for Dissolved and Particulate *trans*-Nonachlor

Tributary	Sampling Dates	Dissolved *Trans*-Nonachlor	Particulate *Trans*-Nonachlor	Total Samples
Fox River	04/07/94 to 10/12/95	38	38	76
Grand Calumet	08/04/94 to 10/18/95	15	15	30
Grand River	04/11/94 to 10/31/95	34	47	81
Kalamazoo	04/12/94 to 10/30/95	38	37	75
Manistique	04/11/94 to 10/26/95	28	27	55
Menominee	04/13/94 to 10/11/95	24	24	48
Milwaukee	03/29/94 to 10/06/95	36	38	74
Muskegon	04/14/94 to 12/05/95	28	28	56
Pere Marquette	04/05/94 to 10/18/95	28	27	55
Sheboygan	04/06/94 to 10/24/95	36	36	72
St. Joseph	04/06/94 to 10/27/95	33	33	66
	Total	338	350	688

The 11 tributaries were chosen for sampling by the Lake Michigan Tributary Coordinating Committee, comprised of representatives from EPA, the Wisconsin Department of Natural Resources, the Michigan Department of Natural Resources, and the U.S. Geological Survey offices in Wisconsin and Michigan. The 11 sites represent the variety of types of river that drain into the Lake Michigan basin. Ten of the eleven rivers were chosen because elevated concentrations of contaminants previously observed in fish collected from these tributaries suggest that these rivers are contributing the highest contaminant loadings to the lake. The exception was the Pere Marquette River in Michigan. This tributary was chosen as the "background" site, with little anthropogenic input. The samples from the Pere Marquette River will be used to estimate loads from the small portion of the Lake Michigan watershed that was not monitored in this study. The 11 monitored tributaries represent greater than 90% of the total river flow into Lake Michigan and an even higher percentage of the total tributary load of pollutants into Lake Michigan (see Section 2.4.2).

The committee classified the tributaries into three categories, based on their "event responsiveness," meaning the degree to which their physical and hydrological characteristics respond to the flow changes associated with precipitation events. The categories were: variable, stable, and super stable. The classifications were used to establish the sampling frequency for each tributary (Table 4-3). All tributaries were to be sampled monthly during the winter and during base (low) flow conditions, with additional samples collected after precipitation events that increased the tributary flow by at least 20%. The planned sampling frequencies were met for all but four of the tributaries (Grand Calumet, Menominee, Milwaukee, and Sheboygan Rivers).

Table 4-3. Tributary Classifications Relative to Responsiveness to Precipitation Events

Tributary	Event Responsiveness	Number of Planned Sampling Events	
		High Flow	Low Flow
Fox River	Stable	18	8
Grand Calumet	Super Stable	16	
Grand River	Stable	24	12
Kalamazoo	Stable	18	8
Manistique	Stable	16	
Menominee	Stable	18	8
Milwaukee	Variable	30	15
Muskegon	Stable	16	
Pere Marquette	Super Stable	11	5
Sheboygan	Variable	30	15
St. Joseph	Stable	18	8

4.1.1 Temporal Variation

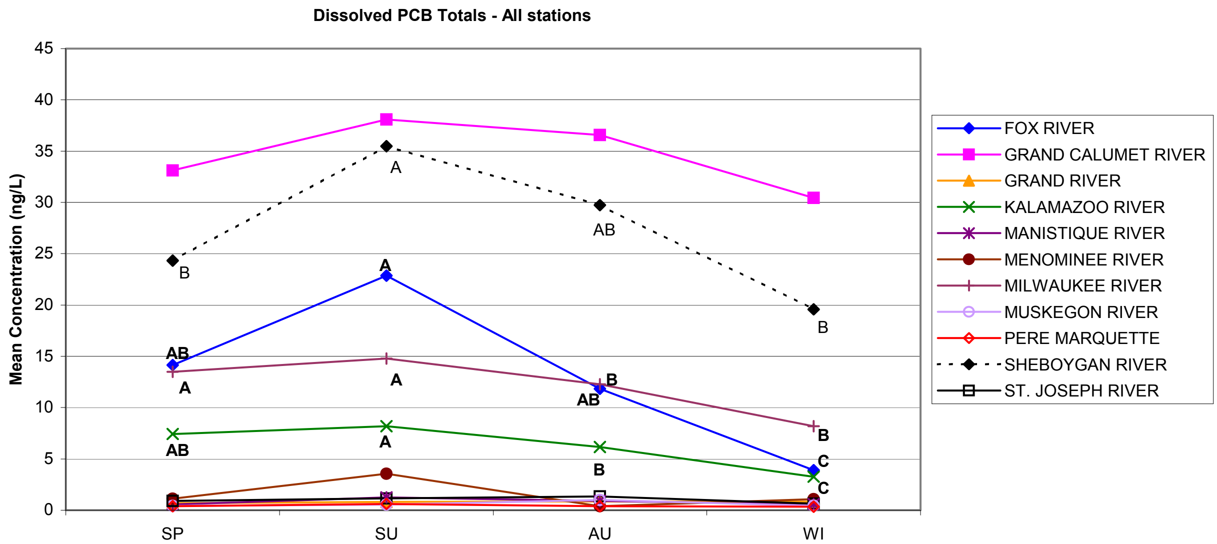
Many of the tributary samples were collected in response to precipitation events and these events may not have occurred simultaneously across the entire Lake Michigan basin. As a result, the collection dates of the samples sometimes vary greatly across the tributaries. Therefore, the tributary results were examined by season, where the seasons were defined as:

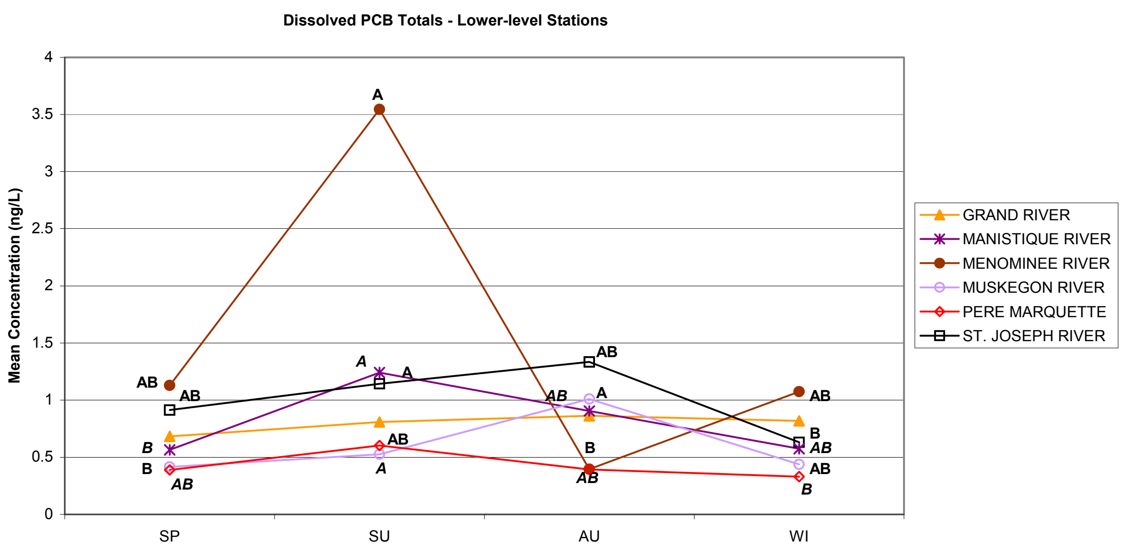
Spring (SP) = March 20 to June 20,
Summer (SU) = June 21 to September 22,
Autumn (AU) = September 23 to December 21, and
Winter (WI) = December 22 to March 19

The concentrations of dissolved and particulate total PCBs exhibited a seasonal trend for many of the tributaries, with higher mean concentrations occurring in summer months and lower mean concentrations occurring in winter months. There were significant differences between seasons for the dissolved total PCB concentrations in nine of the eleven tributaries, and significant differences between season for the particulate total PCB concentration in six of the eleven tributaries. However, the trend was not consistent across all of the tributaries. Based on F-tests of log-transformed concentration data, there were significant interactions between tributary and season. The temporal variations in the dissolved and particulate concentrations of individual PCB congeners did not exhibit trends that were consistent across all tributaries, based on F-tests of log-transformed concentration data.

The mean seasonal concentrations of dissolved and particulate total PCBs across all 11 tributaries span at least two orders of magnitude. The tributaries can be visually divided into two groups, based on PCB concentration. Specifically, six of the eleven tributaries exhibit dissolved and particulate total PCB mean concentrations that are less than 4 ng/L, and often less than 1 ng/L, across all four seasons. The results are plotted separately for dissolved total PCBs (Figure 4-1) and particulate total PCBs (Figure 4-2).

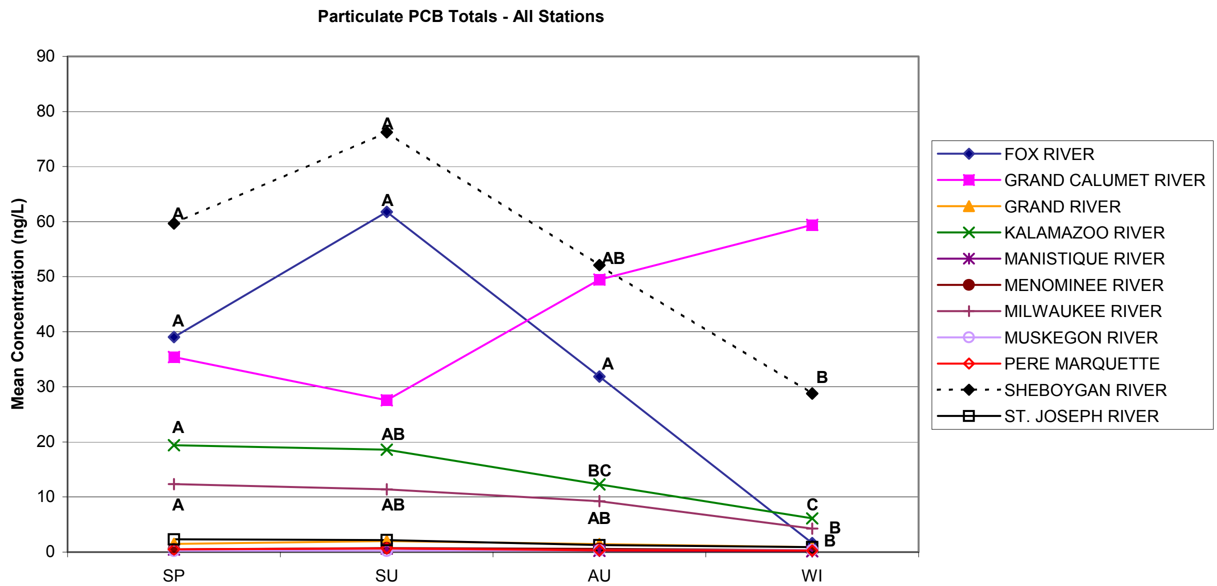
Figure 4-1. Temporal Variation in Total Dissolved PCB Concentrations Measured in Lake Michigan Tributaries

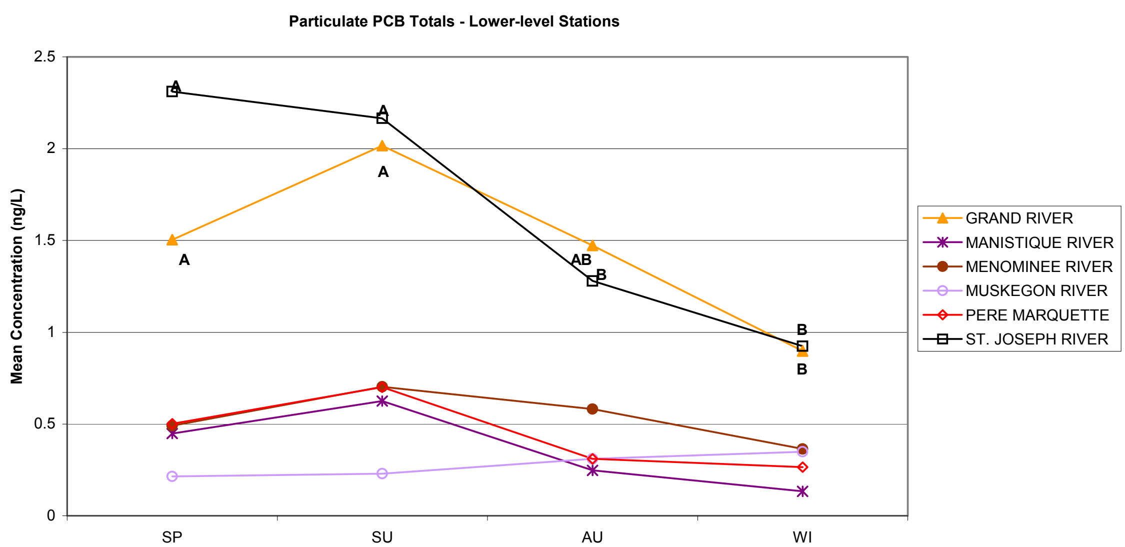




Note: The letters (A - C) represent the results of the analysis of variance and multiple comparisons test. Points with the same letter were not statistically different (at alpha = 0.05). Tributaries without letters are those where there were no significant differences between seasons.

Figure 4-2. Temporal Variation in Total Particulate PCB Concentrations Measured in Lake Michigan Tributaries





Note: The letters (A - B) represent the results of the analysis of variance and multiple comparisons test. Points with the same letter were not statistically different (at alpha = 0.05). Tributaries without letters are those where there were no significant differences between seasons.

The mean dissolved total PCB concentrations appear to peak in summer in three of the tributaries (Fox, Menominee, and Sheboygan), while they appear to peak in the autumn for three other tributaries (Grand River, Muskegon, and St. Joseph). However, for many of the tributaries, the results do not show significant differences between seasons and those apparent peaks are not significantly different from the mean concentrations of the adjacent seasons. For example, the seasonal mean dissolved total PCB concentrations in the Grand Calumet River and the Grand River are not statistically significant different between any of the seasons. For Fox River and Kalamazoo River, the mean concentrations in spring and summer are not significantly different, but the mean concentration in summer is significantly higher than in autumn, which is significantly higher than in winter.

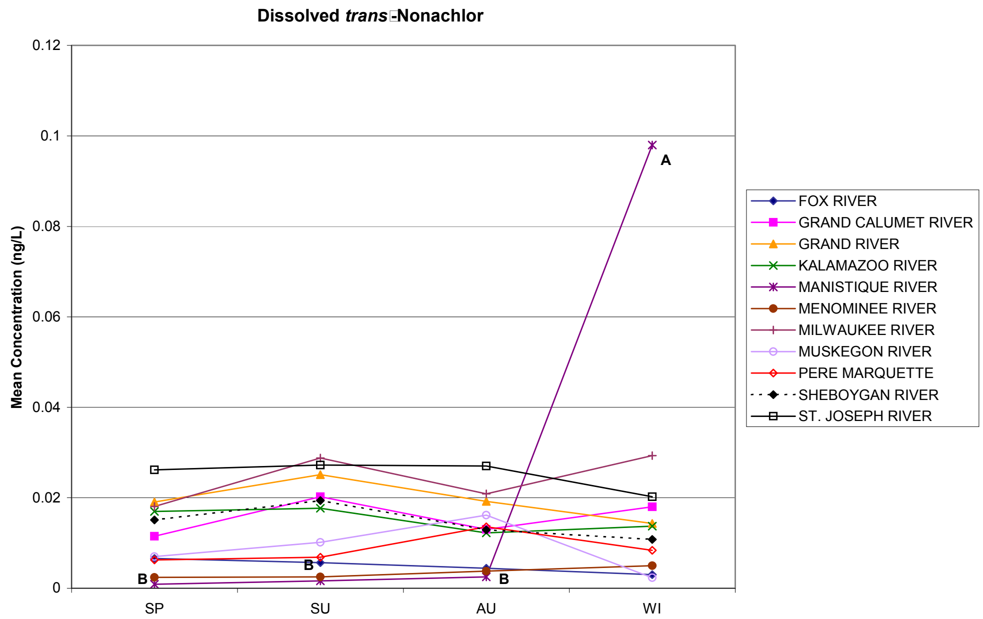
The summer mean concentration of dissolved total PCBs in the Menominee River is significantly different from the autumn mean concentration, but neither the summer nor the autumn mean is significantly different from the spring and winter means. The large increase in concentration that is visible in Figure 4-1 is driven by one of the four summer results for this tributary, with a dissolved total PCB result of 10.6 ng/L. There is no unambiguous evidence that indicates this high result for total dissolved PCBs is due to contamination in the field or the laboratory, thus the result was not excluded from the database. However, examination of the data qualifiers applied to the individual PCB congener results by both the PI who produced the results and the data reviewers suggest some increased uncertainty with this specific sample (e.g., PCB 33 was associated with a field blank that did not meet the acceptance criteria and PCB 180 was reported with the suspected contamination flag), but these concerns did not affect a large number of other congeners. Were this result excluded from the calculation of the mean seasonal results, the mean summer result for dissolved total PCBs at the Menominee River would be on the order of 1.1 ng/L, a value well in line with the other low-level stations.

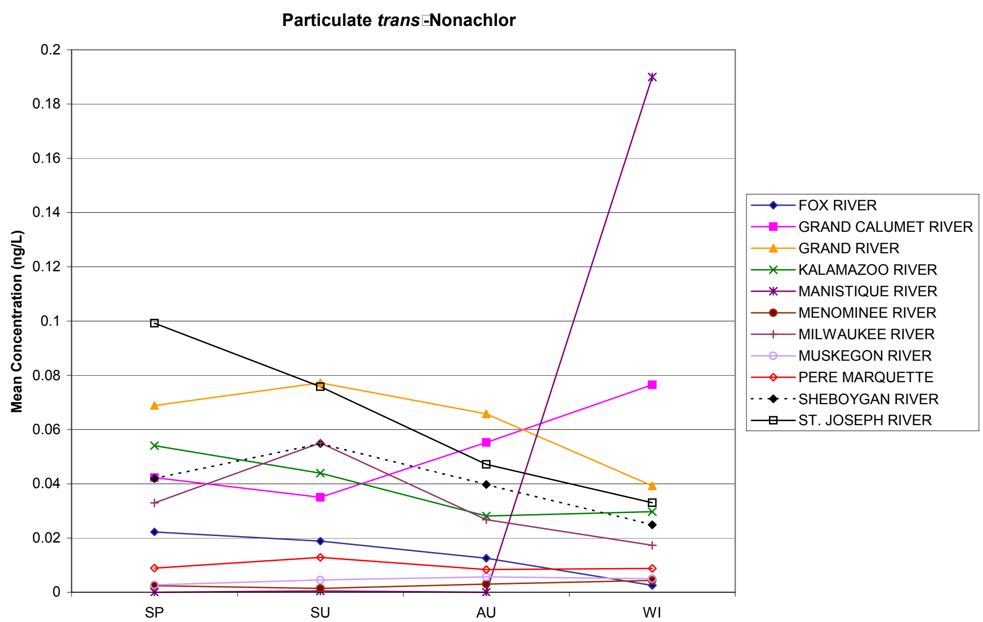
The mean particulate total PCB concentrations appear to peak in either spring or summer in 9 of the 11 tributaries, with the lowest mean concentrations in the winter. However, the significance of the seasonal differences varies by tributary. For example, in the Sheboygan River, the mean spring and summer particulate total PCB concentrations are not significantly different from one another, but both are significantly different from the winter mean concentration. In the Fox River, mean spring, summer, and autumn particulate total PCB concentrations are not significantly different from one another, but all are significantly different from the mean winter concentration. For the Kalamazoo, Milwaukee, Grand, and St. Joseph Rivers, the spring mean particulate total PCB concentrations are never the lowest concentrations of the four seasons and the winter concentrations are never the highest of the four seasons.

Despite the apparent increase in the mean total particulate PCB concentrations from summer to winter in Figure 4-2 for the Grand Calumet River, there is no statistically significant difference across all four seasons in this tributary. Among the six low-level tributaries, there are no significant differences among the seasons for the mean particulate total PCB concentrations in the Manistique, Menominee, Muskegon, and Pere Marquette Rivers.

The mean concentrations of dissolved and particulate *trans*-nonachlor show fewer significant differences than the total PCB results (Figure 4-3). Eight of the eleven tributaries (Fox, Grand Calumet, Grand, Menominee, Milwaukee, Muskegon, Pere Marquette, and St. Joseph) exhibit no statistically significant differences in mean dissolved *trans*-nonachlor concentrations among the seasons. Of the other three tributaries, the mean dissolved *trans*-nonachlor in the Kalamazoo River is never the lowest in spring or summer, and never the highest in autumn, while in the Sheboygan River, mean dissolved *trans*-nonachlor is never the lowest in the summer, or the highest in the winter. The dissolved *trans*-nonachlor results for the Manistique River are characterized by a very high mean concentration in the winter which is significantly different from the other three seasons, which in turn, are not significantly different from one another. The very high winter mean concentration is repeated in the particulate *trans*-nonachlor results in this tributary. Figure 4-4 illustrates the seasonal trends for dissolved and particulate *trans*-nonachlor in the tributaries after removing the very high winter mean result for the Manistique River.

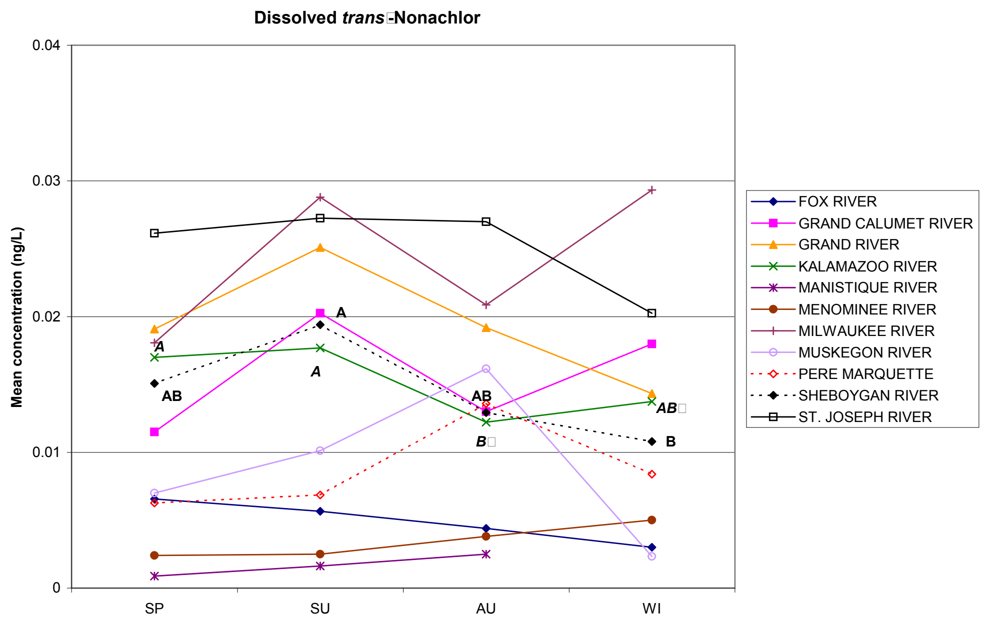
Figure 4-3. Temporal Variation in Total Dissolved (top) and Particulate (bottom) *trans*-Nonachlor Concentrations Measured in Lake Michigan Tributaries

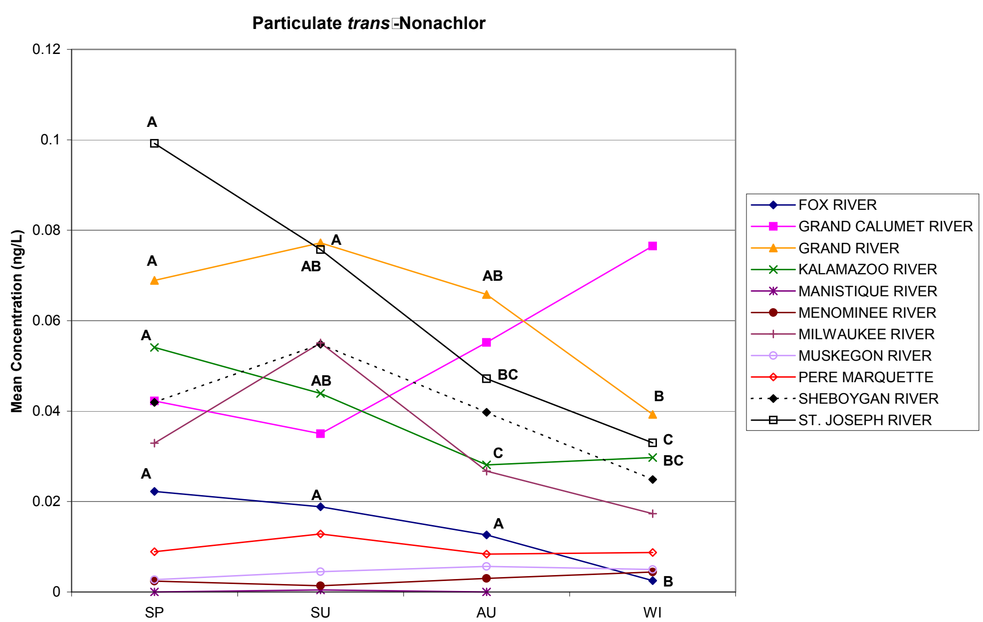




Note: The letters (A - B) represent the results of the analysis of variance and multiple comparisons test. Points with the same letter were not statistically different (at alpha = 0.05). Tributaries without letters are those where there were no significant differences between seasons.

Figure 4-4. Temporal Variation in Total Dissolved (top) and Particulate (bottom) *trans*-Nonachlor Concentrations Measured in Lake Michigan Tributaries without the Winter Mean for the Manistique River





Note: The letters (A - B) represent the results of the analysis of variance and multiple comparisons test. Points with the same letter were not statistically different (at alpha = 0.05). Tributaries without letters are those where there were no significant differences between seasons.

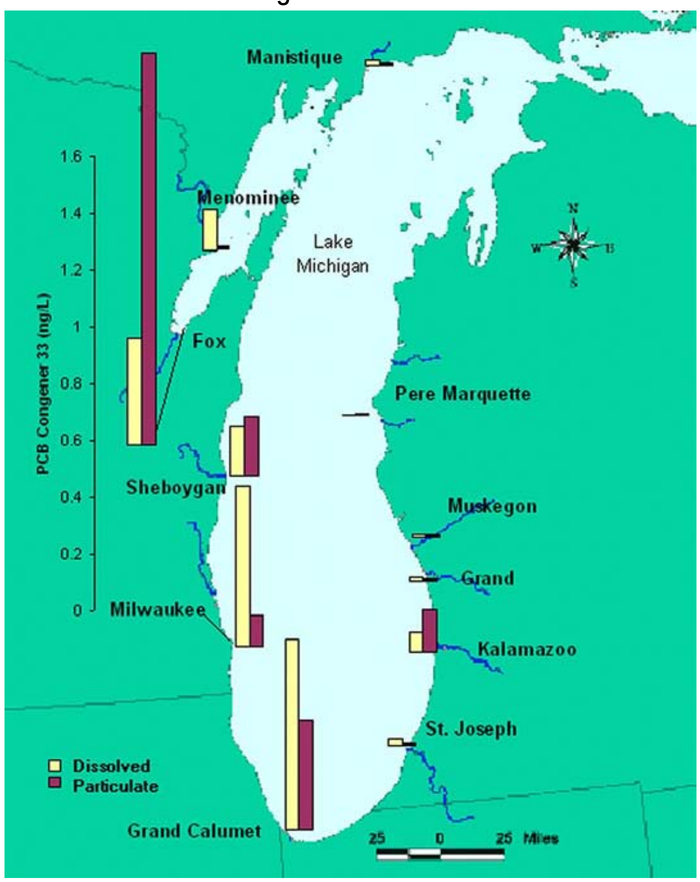
Six of the tributaries (Grand Calumet, Menominee, Milwaukee, Muskegon, Pere Marquette, and Sheboygan) exhibited no statistically significant differences in the particulate *trans*-nonachlor concentrations across seasons. The Manistique River had one non-zero result in summer and one non-zero result in winter, and all other results were reported as zero. As seen in the dissolved *trans*-nonachlor result, the winter mean particulate concentration in the Manistique River was much higher than for any other tributary. The bottom portion of Figure 4-4 shows the results for the tributaries without this high mean particulate result.

The trends for the other four tributaries are such that the mean particulate *trans*-nonachlor concentrations in the spring were never the lowest, and the winter mean concentrations were never the highest.

4.1.2 Geographical Variation

The concentrations of dissolved and particulate PCBs and *trans*-nonachlor varied by tributary over the course of the study (Tables 4-4 through 4-8). For example, the concentration of dissolved PCB 33 ranged from 0 to 1.1 ng/L and the concentration of particulate PCB 33 ranged from 0 to 4.2 ng/L. The mean dissolved concentrations of PCB 33 ranged from 0.0067 ng/L in the Pere Marquette River to 0.76 ng/L in the Grand Calumet River, while the mean particulate concentration of PCB 33 ranged from 0.00042 ng/L in the Pere Marquette River to 1.5 ng/L in the Fox River (Figure 4-5). (The particulate PCB 33 results were reported as zero for all 27 samples from the St. Joseph River).

Figure 4-5. Mean Dissolved and Particulate Concentrations of PCB 33 in Lake Michigan Tributaries

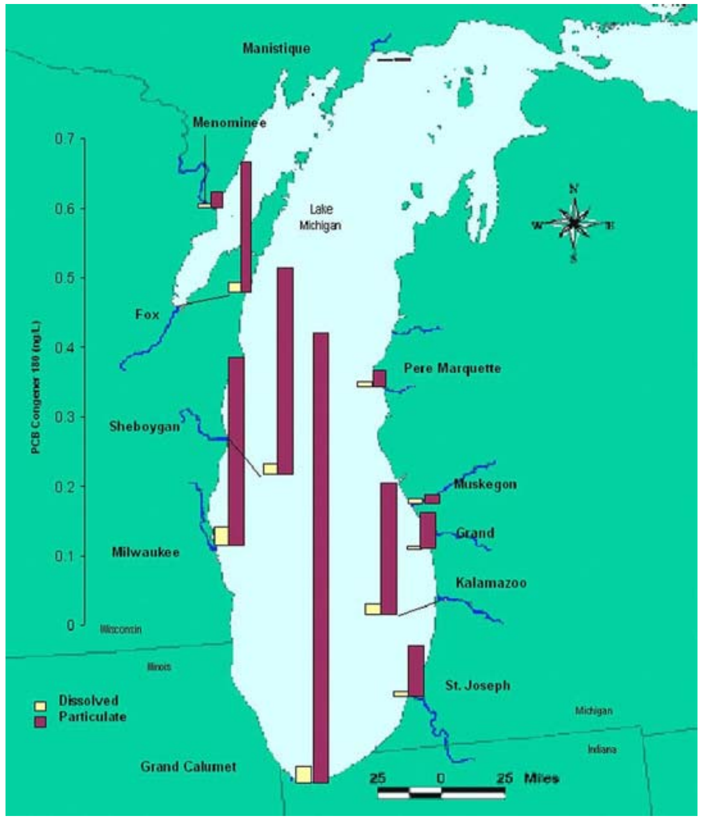


Other PCB congeners exhibited ranges and mean concentrations similar to those observed for PCB 33. The dissolved total PCB concentrations ranged from 0 ng/L in four tributaries to 48 ng/L in the Grand Calumet, while particulate total PCB concentrations ranged from 0 ng/L in four tributaries to 120 ng/L in the Sheboygan River. Mean dissolved total PCB concentrations ranged from 0.43 ng/L in the Pere Marquette River to 35 ng/L in the Grand Calumet, while mean particulate concentration ranged from 0.25 ng/L in the Muskegon River to 55 ng/L in the Sheboygan River.

For PCB 33, the mean dissolved concentrations are higher than the mean particulate concentrations in eight of the eleven tributaries (Figure 4-5), while the particulate concentrations are higher in the Fox, Kalamazoo, and Sheboygan Rivers. The distribution between the dissolved and particulate fractions appears to change for the higher molecular weight congeners (e.g., see Figure 4-6 for the mean concentrations of PCB 180). For PCB 118, the mean concentrations of the particulate samples were markedly higher than the dissolved concentrations in 9 of the 11 tributaries and essentially equal in the

Menominee and Muskegon Rivers (Table 4-5). For PCB 180, the mean concentrations of the particulate samples were markedly higher than the dissolved concentrations in all 11 tributaries.

Figure 4-6. Mean Dissolved and Particulate Concentrations of PCB 180 in Lake Michigan Tributaries



Concentrations of dissolved *trans*-nonachlor ranged from 0 in seven tributaries to 0.19 ng/L in the Manistique River, while particulate *trans*-nonachlor ranged from 0 in five tributaries to 0.38 ng/L in the Manistique River (Table 4-9). (Note: The maximum dissolved and particulate *trans*-nonachlor concentrations occurred in the same sample from the Manistique River, which is otherwise relatively uncontaminated. These two values may be the result of contamination of the sample during collection).

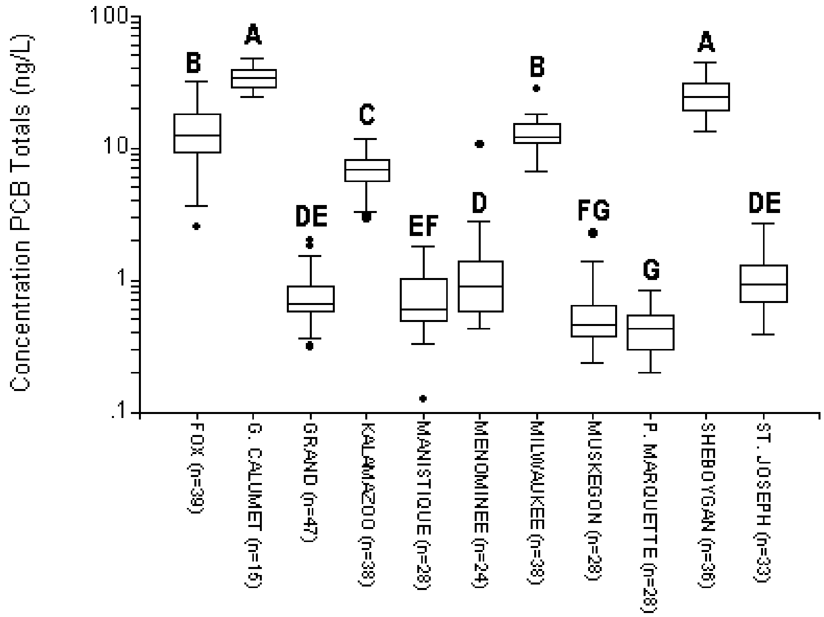
Mean dissolved *trans*-nonachlor concentrations ranged 0.0033 ng/L in the Menominee River to 0.026 ng/L in the St. Joseph River, while mean particulate *trans*-nonachlor concentrations ranged from 0.0028 ng/L in the Menominee River to 0.074 ng/L in the St. Joseph River.

There are statistically significant differences among the mean concentrations of dissolved and particulate PCBs in the 11 tributaries. The differences in the mean dissolved concentrations of total PCBs are shown in Figure 4-7. The mean dissolved total PCB concentrations in the Grand Calumet and Sheboygan Rivers were significantly higher than in all other tributaries. The mean dissolved total PCB concentrations in the Pere Marquette River were significantly lower than in all other tributaries except the Muskegon River. There is a statistically significant interaction between tributary and year for the particulate total PCB results ($p=0.0118$, two-way ANOVA, total PCB concentrations were log-transformed prior to conducting the test). Therefore, the mean particulate total PCB concentrations for all of the tributaries are presented separately for 1994 and 1995 (Figure 4-8, top and bottom, respectively).

There was a statistically significant difference between the particulate total PCB concentrations from 1994 and 1995 at three of the 11 tributaries (Fox, Grand, and Muskegon Rivers), based on two-sample *t*-tests of log-transformed PCB data. The mean particulate total PCB concentrations were significantly higher in 1994 than in 1995 in the Fox and Grand Rivers, while in the Muskegon River, the 1995 mean concentration was higher than in 1994. The differences between the results in 1994 and 1995 in these three tributaries may be a function of the unequal distribution of samples across calendar years (e.g., there are no 1994 data before April and no 1995 data after October), or the differences may be the result of some other factors.

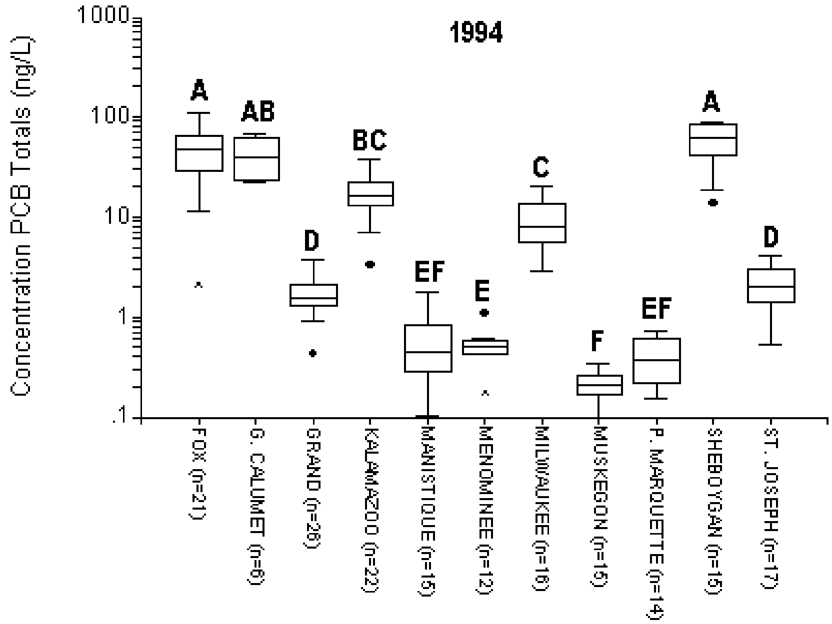
The distinction of the "lower-level" tributaries shown in Figure 4-2 also holds true when the same dissolved and particulate total PCB results were used in Figures 4-7 and 4-8. The six tributaries with relatively low concentrations of dissolved and particulate PCBs (Grand, Manistique, Menominee, Muskegon, Pere Marquette, and St. Joseph) in Figure 4-2 can also be distinguished from the five tributaries with much higher mean concentrations (Fox, Grand Calumet, Kalamazoo, Milwaukee, and Sheboygan) in Figures 4-7 and 4-8.

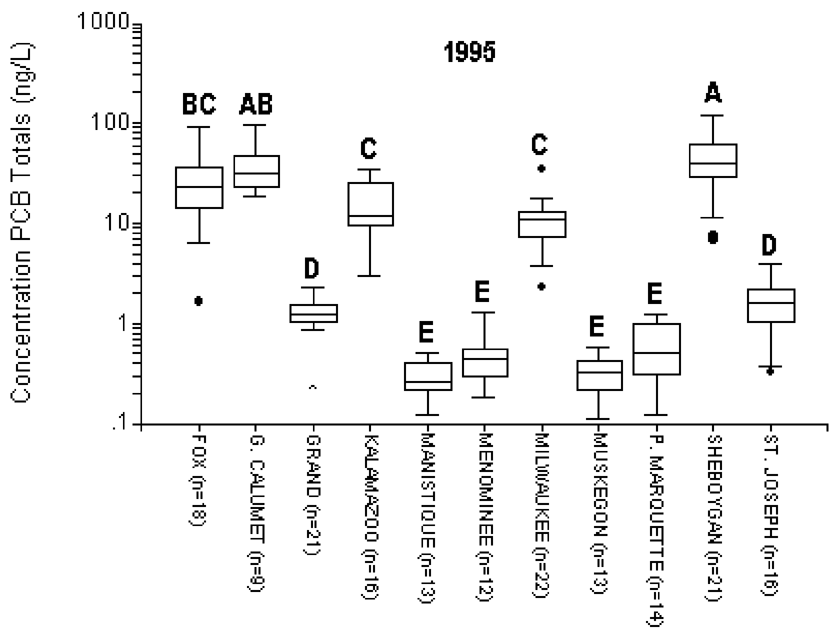
Figure 4-7. Mean Dissolved Total PCB Concentrations in Lake Michigan Tributaries



Concentration is plotted on a log scale. Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The letters (A - G) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

Figure 4-8. Mean Particulate Total PCB Concentrations in Lake Michigan Tributaries in 1994 (top) and 1995 (bottom)

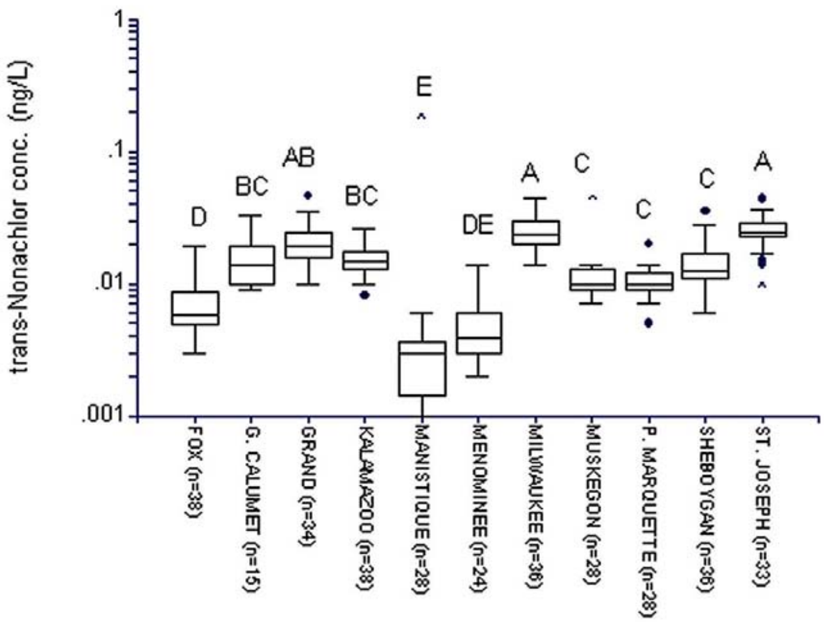




Concentration is plotted on a log scale. Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The ^s represent results beyond 3*IQR from the box. The letters (A - F) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

The results for *trans*-nonachlor exhibited less distinct geographical variations, compared to the PCB results (Figure 4-9). For example, the concentrations of dissolved *trans*-nonachlor did not exhibit the distinction of the "lower-level" tributaries shown in Figure 4-2 for the PCB results. Only two of those six "lower-level" tributaries had statistically lower dissolved *trans*-nonachlor concentrations: the Manistique and Menoninee Rivers. In marked contrast to the dissolved PCB results, the dissolved *trans*-nonachlor results for the Fox River were the third lowest of the 11 tributaries.

Figure 4-9. Mean Dissolved *trans*-Nonachlor Concentrations in Lake Michigan Tributaries

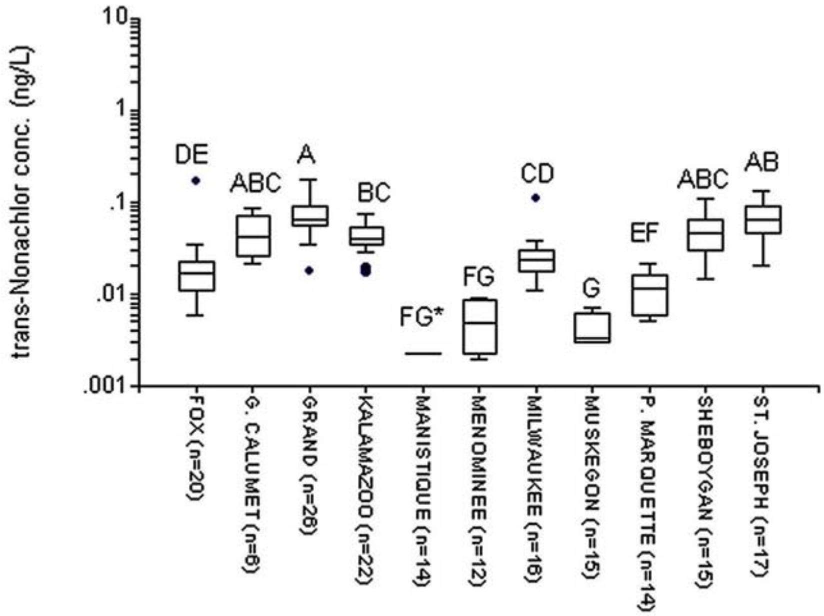


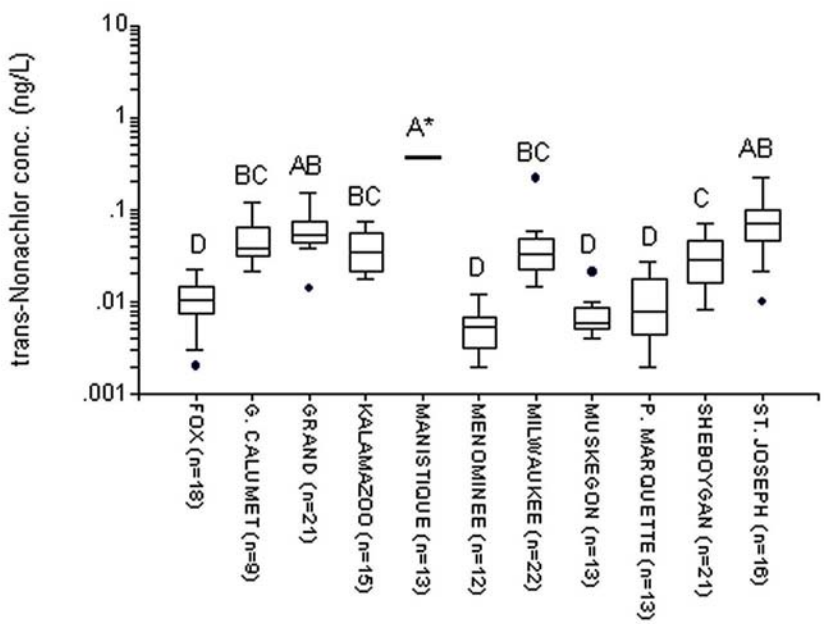
Concentration is plotted on a log scale. Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The ^s represent results beyond 3*IQR from the box. The letters (A - E) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

As with the particulate PCB results, there is a statistically significant interaction between tributary and year for the particulate *trans*-nonachlor results (p=0.0001, two-way ANOVA, *trans*-nonachlor concentrations were log-transformed prior to conducting the test). Therefore, the mean particulate *trans*-nonachlor concentrations for all of the tributaries are presented separately for 1994 and 1995 (Figure 4-10, top and bottom, respectively).

However, unlike the particulate PCB results, the distinctions between rivers with relatively low or relatively high concentrations of particulate *trans*-nonachlor are not as clear, nor as consistent between the two years. For example, the particulate *trans*-nonachlor results for the Fox River are not statistically different from those in the Pere Marquette River in either 1994 or 1995. The concerns about the anomalous particulate *trans*-nonachlor in the Manistique River are evident in the top and bottom portions of Figure 4-10, where the 1994 mean result is among the lowest of all 11 tributaries, while the 1995 mean result is the highest of all 11 tributaries.

Figure 4-10. Mean Particulate *trans*-Nonachlor Concentrations in Lake Michigan Tributaries in 1994 (top) and 1995 (bottom)





Concentration is plotted on a log scale. Boxes represent the 25th percentile (bottom of box), 50th percentile (center line), and 75th percentile (top of box) results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. The *s represent instances where all but one observation was zero (0) and the log of 0 is indeterminate. The letters (A - G) above the boxes represent the results of the analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

Table 4-4. Concentrations of PCB Congener 33 Measured in Tributaries

Fraction	Tributary	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
Dissolved	Fox River	39	0.43	0.066 to 0.93	0.23	55	0.0
	Grand Calumet	15	0.76	0.39 to 1.1	0.27	36	0.0
	Grand River	35	0.018	0.0 to 0.043	0.0099	55	23
	Kalamazoo	36	0.095	0.035 to 0.17	0.032	34	0.0
	Manistique	24	0.0099	0.0 to 0.028	0.0098	99	50
	Menominee	15	0.082	0.015 to 0.56	0.14	170	20
	Milwaukee	37	0.27	0.094 to 0.94	0.14	52	0.0
	Muskegon	24	0.010	0.0 to 0.067	0.018	170	71
	Pere Marquette	27	0.0067	0.0 to 0.025	0.0087	129	93
	Sheboygan	28	0.20	0.12 to 0.31	0.058	29	0.0
	St. Joseph	28	0.020	0.0 to 0.052	0.015	74	50
Particulate	Fox River	39	1.5	0.067 to 4.2	0.99	64	0.0
	Grand Calumet	15	0.46	0.18 to 1.1	0.26	57	0.0
	Grand River	25	0.0033	0.0 to 0.026	0.0070	210	84
	Kalamazoo	34	0.16	0.023 to 0.38	0.092	56	0.0
	Manistique	27	0.0016	0.0 to 0.0090	0.0029	180	100
	Menominee	24	0.00076	0.0 to 0.018	0.0037	490	100
	Milwaukee	34	0.12	0.032 to 0.36	0.068	56	0.0
	Muskegon	28	0.00088	0.0 to 0.012	0.0027	310	100
	Pere Marquette	28	0.00042	0.0 to 0.0083	0.0017	400	100
	Sheboygan	16	0.25	0.048 to 0.46	0.12	47	0.0
	St. Joseph	27	0.0	0.0 to 0.0	0.0	--	100

Table 4-5. Concentrations of PCB Congener 118 Measured in Tributaries

Fraction	Tributary	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
Dissolved	Fox River	39	0.044	0.014 to 0.14	0.022	51	7.7
	Grand Calumet	15	0.14	0.083 to 0.25	0.044	31	0.0
	Grand River	45	0.013	0.0 to 0.028	0.0052	41	31
	Kalamazoo	38	0.058	0.026 to 0.14	0.023	39	0.0
	Manistique	27	0.0039	0 to 0.011	0.0034	88	93
	Menominee	22	0.014	0.0058 to 0.040	0.0074	51	91
	Milwaukee	37	0.072	0.037 to 0.19	0.026	36	0.0
	Muskegon	28	0.0068	0.0 to 0.019	0.0064	94	100
	Pere Marquette	27	0.0062	0.0 to 0.028	0.0065	110	96
	Sheboygan	36	0.19	0.084 to 0.31	0.058	30	0.0
	St. Joseph	32	0.021	0.0095 to 0.039	0.0082	38	50
Particulate	Fox River	39	0.43	0.014 to 1.2	0.26	60	2.6
	Grand Calumet	15	0.83	0.20 to 1.7	0.46	55	0.0
	Grand River	47	0.065	0.0045 to 0.14	0.026	40	2.1
	Kalamazoo	36	0.47	0.088 to 0.98	0.24	51	0.0
	Manistique	27	0.010	0.0 to 0.032	0.0080	78	63
	Menominee	23	0.015	0.0 to 0.030	0.0076	51	70
	Milwaukee	38	0.20	0.030 to 0.60	0.13	62	0.0
	Muskegon	28	0.0068	0.0 to 0.014	0.0035	51	100
	Pere Marquette	28	0.017	0.0 to 0.046	0.013	74	64
	Sheboygan	36	1.9	0.22 to 4.2	1.1	57	0.0
	St. Joseph	32	0.083	0.0 to 0.2	0.045	54	9.4

Table 4-6. Concentrations of PCB Congener 180 Measured in Tributaries

Fraction	Tributary	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
Dissolved	Fox River	38	0.013	0.0 to 0.044	0.0088	69	68
	Grand Calumet	14	0.022	0.0 to 0.081	0.019	86	36
	Grand River	42	0.0029	0.0 to 0.010	0.0026	90	95
	Kalamazoo	37	0.014	0.0 to 0.056	0.010	66	57
	Manistique	28	0.0015	0.0 to 0.014	0.0029	190	96
	Menominee	21	0.0052	0.0 to 0.024	0.0060	110	100
	Milwaukee	38	0.023	0.011 to 0.11	0.016	70	21
	Muskegon	28	0.0076	0.0 to 0.023	0.0070	93	89
	Pere Marquette	28	0.0054	0.0 to 0.020	0.0059	110	96
	Sheboygan	36	0.016	0.0 to 0.055	0.011	67	50
	St. Joseph	32	0.0065	0.0 to 0.023	0.0068	110	91
Particulate	Fox River	39	0.20	0.011 to 0.50	0.12	58	5.1
	Grand Calumet	15	0.66	0.32 to 1.5	0.33	50	0.0
	Grand River	44	0.049	0.0093 to 0.13	0.023	46	0.0
	Kalamazoo	36	0.19	0.046 to 0.36	0.086	45	0.0
	Manistique	25	0.0031	0.0 to 0.010	0.0031	100	92
	Menominee	24	0.026	0.0 to 0.12	0.025	95	42
	Milwaukee	38	0.28	0.086 to 1.1	0.17	61	0.0
	Muskegon	27	0.012	0.0 to 0.027	0.0070	61	85
	Pere Marquette	26	0.018	0.0 to 0.063	0.015	84	58
	Sheboygan	36	0.30	0.045 to 0.91	0.18	59	0.0
	St. Joseph	31	0.074	0.016 to 0.15	0.032	43	6.5

Table 4-7. Concentrations of Total PCBs Measured in Tributaries

Fraction	Tributary	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)
Dissolved	Fox River	39	14	2.5 to 32	7.6	53
	Grand Calumet	15	35	24 to 48	6.5	19
	Grand River	47	0.76	0.0 to 2.0	0.35	47
	Kalamazoo	38	6.9	2.9 to 12	2.1	30
	Manistique	28	0.76	0.13 to 1.8	0.39	52
	Menominee	24	1.4	0.0 to 11	2.1	150
	Milwaukee	38	13	6.7 to 28	4.0	30
	Muskegon	28	0.58	0.23 to 2.2	0.40	69
	Pere Marquette	28	0.43	0.0 to 0.83	0.19	45
	Sheboygan	36	26	13 to 45	8.3	32
	St. Joseph	33	1.0	0.0 to 2.7	0.53	52
Particulate	Fox River	39	39	1.6 to 110	25	64
	Grand Calumet	15	41	19 to 96	22	53
	Grand River	47	1.6	0.24 to 3.7	0.63	40
	Kalamazoo	38	16	0.0 to 38	9.6	59
	Manistique	28	0.41	0.046 to 1.8	0.37	90
	Menominee	24	0.52	0.18 to 1.3	0.27	53
	Milwaukee	38	11	2.3 to 35	6.2	58
	Muskegon	28	0.25	0.0 to 0.59	0.14	54
	Pere Marquette	28	0.47	0.0 to 1.2	0.32	67
	Sheboygan	36	55	6.9 to 120	31	56
	St. Joseph	33	1.9	0.0 to 4.1	0.98	52

Table 4-8. Concentrations of *trans*-Nonachlor Measured in Tributaries

Fraction	Tributary	N	Mean (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	% Below DL
Dissolved	Fox River	38	0.0056	0.0 to 0.019	0.0050	89	97
	Grand Calumet	15	0.015	0.0090 to 0.033	0.0067	44	67
	Grand River	34	0.020	0.0 to 0.046	0.0083	40	2.9
	Kalamazoo	38	0.016	0.0080 to 0.026	0.0040	26	74
	Manistique	28	0.0083	0.0 to 0.19	0.036	430	96
	Menominee	24	0.0033	0.0 to 0.014	0.0036	110	100
	Milwaukee	36	0.023	0.0 to 0.044	0.0093	41	25
	Muskegon	28	0.0094	0.0 to 0.046	0.0088	94	96
	Pere Marquette	28	0.0081	0.0 to 0.020	0.0054	67	96
	Sheboygan	36	0.015	0.0060 to 0.035	0.0057	39	81
	St. Joseph	33	0.026	0.010 to 0.045	0.0071	28	15
Particulate	Fox River	38	0.018	0.0 to 0.17	0.026	145	74
	Grand Calumet	15	0.049	0.021 to 0.12	0.028	56	0.0
	Grand River	47	0.067	0.014 to 0.18	0.030	44	0.0
	Kalamazoo	37	0.042	0.017 to 0.076	0.016	39	2.7
	Manistique	27	0.014	0.0 to 0.38	0.073	520	96
	Menominee	24	0.0028	0.0 to 0.012	0.0035	130	100
	Milwaukee	38	0.037	0.011 to 0.22	0.035	96	18
	Muskegon	28	0.0041	0.0 to 0.021	0.0047	110	96
	Pere Marquette	27	0.0098	0.0 to 0.027	0.0075	76	85
	Sheboygan	36	0.040	0.0082 to 0.11	0.024	58	19
	St. Joseph	33	0.074	0.010 to 0.23	0.043	57	3.0

4.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the PCBs and *trans*-nonachlor monitoring portion of the study are further described in Section 2.7 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB quality assurance program is provided in the Lake Michigan Mass Balance Study Quality Assurance Report (USEPA, 2001b). A brief summary of data quality issues for the tributary PCBs and *trans*-nonachlor data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.5, because data comparability was important to the successful development of the mass balance model, the PIs used similar sample collection, extraction, and analysis methods for the PCB and trans-nonachlor monitoring in this study. However, as noted earlier in this section, after the study began, changes were made to the procedures used for cleaning the XAD-2® resin and for the analyses of the tributary samples. The first 35 field samples were analyzed on an older GC/ECD system and were quantified against the Aroclor mixture prepared in 1985 by Dr. Mike Mullin at the EPA-Grosse Ile laboratory. These samples are identified in the data set with the text "Method 1293-11/11/94" in the Exception to Method text field. After mid-November 1994, analyses were performed on a new GC/ECD system that resulted in resolution of more PCB congeners (78 vs. 65) and lower method detection limits (MDLs) than in the earlier analyses. In addition, samples analyzed after mid-November 1994 were quantified against the 1994 version of the Mullin mix standard prepared exclusively for the LMMB Study. These analytical changes were implemented after November 12, 1994, but affect all the tributary samples collected from May 1994 to the end of the LMMB Study.

As discussed in Section 2.7, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 4-9 provides a summary of flags applied to the tributary PCB and *trans*-nonachlor data. The summary includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.7. Compared to other matrices, the percentage of results that were qualified for these criteria is relatively small.

PIs used surrogate spikes to monitor the bias of the analytical procedure. The PCB results were corrected for the recoveries of the surrogates. The *trans*-nonachlor results were *not* surrogate-corrected. Only 0.6% of the results of the tributary samples analyzed for dissolved PCB 33 (2 samples) were qualified for surrogate recovery problems (Table 4-9).

Laboratory matrix spike samples also were used to monitor the bias of the analytical procedure. The laboratory matrix spike samples were prepared from unexposed filters and XAD-2® cartridges that were spiked with PCBs and *trans*-nonachlor. The results for the matrix spike samples were compared to the MQO for spike recoveries (50 - 125%). Analytical results associated with matrix spike samples with recoveries below the MQO limits were flagged with failed matrix spike and low bias and results associated with matrix spike samples with recoveries higher than the MQO limits were flagged with failed matrix spike and high bias. Analytical results were considered invalid and flagged as such when the analyte was undetected and recoveries for associated matrix spike samples were less than 10%. No tributary *trans*-nonachlor samples failed the matrix spike MQOs. Overall, only 1.4% of the samples were associated with a matrix spike samples that failed the MQOs for a given PCB congener. None of the results for PCBs 33, 118, or 180 were flagged as failing the matrix spike MQOs.

Field blanks were collected for PCBs and *trans*-nonachlor. When field blank contamination was greater than 3.3 times the method detection limit, all of the associated results were flagged with the failed field blank sample code (FRB). Field blanks were not collected at all stations, so potential station-specific contamination associated with these sites cannot be evaluated. However, contamination associated with sample collection and sampling equipment and sample processing, shipping, storing, and analyzing can be evaluated based on the field blanks collected throughout the study. For dissolved PCB 33, 3% of the field samples were associated with a field blank in which this congener was reported above the sample-specific detection limit (Table 4-9). None of the field samples results for *trans*-nonachlor were qualified because of field blank results.

Two types of laboratory blanks were prepared and analyzed for PCBs and *trans*-nonachlor. One type of laboratory blank (LRB) consisted of an unexposed resin cartridge and filter that were extracted like a field sample. Another type of laboratory blank (LDB) consisted of a volume of solvent processed through an empty Soxhlet apparatus in the same fashion used to extract the field samples. After extraction, the solvent was concentrated and analyzed like a field sample. The results for both types of laboratory blanks were handled in the same fashion. When laboratory blank contamination was greater than the method detection limit, all of the associated results were flagged. None of the field samples results for *trans*-nonachlor were qualified because of laboratory blank results.

PCB congeners were reported detected in all of the laboratory blanks that were analyzed. The following PCB congeners were detected in LDB (empty Soxhlet) blanks above the MDL: 15+17, 18, 87, 170+190, 180, and 206. The following PCB congeners were detected in LRB (unused resin cartridge and filter) blanks above the MDL: 28+31, 41+71+64, 44, 49, 52, 87, 95, 101, 170+190, 180, 194, 208+195, 201 and 206. The differences between the results for these two types of laboratory blanks provide an indication of the congeners that are contributed by the resin and filter, as opposed to the laboratory glassware. The resin and the filter appear to contribute congeners 28+31, 41+71+64, 44, 49, 52, 95, 101, 194, 208+195, and 201.

Trip blanks were prepared and analyzed for PCBs and *trans*-nonachlor. When trip blank contamination was greater than 3.3 times the method detection limit, all of the associated results were flagged with failed trip blank sample code (FFT). For dissolved PCB 33, 7% of the field samples were associated with a trip blank in which this congener was reported above 3.3 times the method detection limit (Table 4-9). None of the field samples were associated with a trip blank that contained *trans*-nonachlor above 3.3 times the method detection limit.

Field duplicates were to be collected at a frequency of 5%. Duplicate samples collected within 5 minutes of each other were considered field duplicates. However, an examination of the field collection records indicated that some of the planned field duplicates were not collected within that 5-minute time frame as a result of problems with equipment mobilization or the time required to pump the sample through the filter and resin cartridge. Those "duplicates" that were collected more than 5 minutes apart were considered "sequential field duplicates" and the data were labeled accordingly (e.g., SDF1 vs. FD1). Combining the field duplicates and sequential field duplicates, the actual rate of collection of duplicates was 4.2%.

The results from the original field sample and the associated duplicate were compared on the basis of the relative percent difference (RPD). The RPD value for each PCB congener and *trans*-nonachlor was compared to the MQO for field duplicate precision. Only 0.3% of the field samples results for PCBs 33 and 180 were qualified because of the field duplicate precision (FFD) concerns (Table 4-9). None of the *trans*-nonachlor results were qualified.

Table 4-9. Summary of Routine Field Sample Flags Applied to Select PCB Congeners and *trans*-Nonachlor in Tributary Samples

Analyte	Fraction	Flags								
		Sensitivity		Contamination		Precision	Bias			
		MDL	UND	FFR	FFT	FFD	FSS	FMS	LOB	HIB
PCB 33	Dissolved	9% (28)	17% (52)	3% (10)	7% (23)	0.3% (1)	0.6% (2)	0	0	0
	Particulate	5% (16)	47% (141)	0	0	0	0	0	0	0
PCB 118	Dissolved	30% (103)	9% (31)	0	0	0	0	0	0	0
	Particulate	21% (72)	4% (14)	0	0	0	0	0	0	0
PCB 180	Dissolved	47% (163)	25% (86)	0	0	0.3% (1)	0	0	0	0
	Particulate	18% (61)	5% (16)	0	0	0	0	0	0	0
trans-Nonachlor	Dissolved	52% (176)	14% (49)	0	0	0	0	0	0	0
	Particulate	26% (93)	15% (53)	0	0	0	0	0	0	0

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

MDL = Less than method detection limit (Analyte produced an instrument response but reported value is below the calculated method detection limit. Validity of reported value may be compromised.)
UND = Analyte not detected (Analyte produced no instrument response above noise.)
FFR = Failed field blank (A field blank sample, type unknown, associated with this analysis failed the acceptance criteria. It is unknown whether the blank that failed was a field blank or a lab blank. Validity of reported value may be compromised.)
FFT = A trip blank associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.
FFD = Failed field duplicate (A field duplicate associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
FSS = Failed surrogate (Surrogate recoveries associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
FMS = Failed matrix spike (A matrix spike associated with this analysis failed the acceptance criteria. Validity of reported value may be compromised.)
LOB = Likely biased low (Reported value is probably biased low as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery or other internal lab QC data. Reported value is not considered invalid.)
HIB = Likely biased high (Reported value is probably biased high as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery, blank contamination, or other internal lab QC data. Reported value is not considered invalid.)

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean relative percent difference (RPD) between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean relative percent difference (RPD) between the results for laboratory duplicate pairs. Table 4-10 provides a summary of data quality assessments for several of these attributes for the tributary PCB and *trans*-nonachlor data.

Because the relative variability of most measurement techniques increases as one approaches the detection limit of the technique, the assessment of the field duplicate results were divided into two concentration regimes. One measure of system precision was calculated for those field duplicate results that were less than 5 times the method detection limit (MDL) of the analyte and a separate measure was calculated for those field duplicate results that were greater than 5 times the MDL.

For PCBs 33 and 118, the dissolved measurements were much more precise for those samples above 5 times the MDL, compared to those samples below 5 times the MDL. The mean relative percent difference (RPD) between the field duplicates decreased from 45% for dissolved PCB 33 field duplicates below 5 times the MDL to 12% for the field duplicates above 5 times the MDL. For PCB 118, the mean RPD dropped from 27% to 3.7% for the dissolved results. There were no field duplicate pairs with dissolved concentrations of PCB 180 or *trans*-nonachlor that were above 5 times the MDL, so a similar comparison is not possible for these two analytes. The precision of the particulate measurements varied much less than that of the dissolved measurements. For particulate PCB 33 in field duplicates, the mean RPD actually increased from 13% for samples below 5 times the MDL to 15% for those duplicates above 5 times the MDL. For PCB 118, the mean RPD decreased from 15% to 10%. For particulate PCB 180, the mean RPDs were 14% and 13% , and they decreased from 13% to 8.6% for particulate *trans*-nonachlor.

Analytical bias was assessed using the results from matrix spike samples. Because it is not practical to prepare a sufficiently large volume (80 - 160 L) of water spiked with known amounts of both dissolved and particulate analytes, the matrix spike samples were prepared in the laboratory by adding known amounts of the PCBs and *trans*-nonachlor to a filter and XAD-2® resin cartridge that had never been exposed in the field and then extracting the filter and the resin using the sample techniques employed for the field samples. The mean recoveries of the analytes were excellent for the PCBs, ranging from 97% to 103% for the PCB congeners in Table 4-10, with no appreciable difference between the dissolved and particulate fractions. The mean recoveries for *trans*-nonachlor were very good, at 86% and 87% for the dissolved and particulate fractions respectively.

Thus, these results demonstrate that the analytical techniques applied to the field samples introduce little or no bias into the PCB results, and a slight low bias into the *trans*-nonachlor results. However, it is not possible to directly assess the capabilities of the sampling techniques to collect the dissolved and particulate analytes from the field samples themselves, a problem that was discussed at length in the quality assurance project plan for the LMMB Study (e.g., it is not practical to prepare large volumes (80 - 160 L) of water containing known concentrations the analytes of interest for routine use as reference samples).

Analytical sensitivity was assessed on the basis of the percentage of study samples that were reported with concentrations below the sample-specific detection limit (SSDL). The sensitivity varied by congener for the PCBs, partly as a function of the analytical instrumentation and its response to the individual congeners.

Table 4-10. Data Quality Assessment for Select PCB Congeners and *trans*-Nonachlor in Tributary Samples

Analyte/Number Field Samples	Parameter	Number of QC samples		Assessment	
		Dissolved	Particulate	Dissolved	Particulate
PCB 33 - 309 Dissolved 297 Particulate	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	9 field duplicate pairs	4 field duplicate pairs	45%	13%
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	13 field duplicate pairs	10 field duplicate pairs	12%	15%
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	64 Matrix Spikes	64 Matrix Spikes	98%	97%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	-	-	24%	53%
PCB 118 - 346 Dissolved 349 Particulate	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	22 field duplicate pairs	10 field duplicate pairs	27%	15%
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	5 field duplicate pairs	19 field duplicate pairs	3.7%	10%
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	64 Matrix Spikes	64 Matrix Spikes	101%	101%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	-	-	37%	24%
PCB 180 - 342 Dissolved 341 Particulate	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	24 field duplicate pairs	11 field duplicate pairs	27%	14%
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	0 field duplicate pairs	18 field duplicate pairs	-	13%
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	64 Matrix Spikes	64 Matrix Spikes	103%	103%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	-	-	69%	22%
trans-Nonachlor - 338 Dissolved 350 Particulate	System Precision - Mean Field Duplicate RPD (%), < 5 * SSDL	26 field duplicate pairs	22 field duplicate pairs	19%	13%
	System Precision - Mean Field Duplicate RPD (%), > 5 * SSDL	0 field duplicate pairs	5 field duplicate pairs	-	8.6%
	Analytical Bias - Mean Laboratory Matrix Spike Recovery (%)	65 Matrix Spikes	65 Matrix Spikes	86%	88%
	Analytical Sensitivity - Samples Reported as < SSDL (%)	-	-	66%	41%

PCB congeners and *trans*-nonachlor were not detected in substantial portions of the dissolved and particulate samples from the tributaries ("UND" flag in Table 4-9). These analytes were detected below the sample-specific detection limits in substantial portions of the samples as well ("MDL" flag in Table 4-9). For the three congeners listed in Table 4-9, the percentage of the samples with results reported below the sample-specific detection limits increases with the congener number (e.g., with molecular weight), suggesting that solubility may play a role in the distribution.

However, other factors affect this assessment of sensitivity, including both the extent of PCB contamination in Lake Michigan and the expected partitioning of analytes between the dissolved and particulate fractions. For example, only 24% of the dissolved PCB 33 results were below the SSDL, while 69% of the dissolved PCB 180 results were below the SSDL. In contrast, 53% of the particulate PCB 33 results were below the SSDL, while only 22% of the particulate PCB 180 results were below the SSDL. These differences between PCB 33 and PCB 180 may reflect the physical properties of the two congeners which indicate that PCB 33 is likely to be more soluble in water than PCB 180 and that PCB 180 is more likely to sorb to particulates. Conversely, the analytical sensitivities reported here may reflect the fact that the mean concentrations of PCB 33 in the tributaries are generally higher than the mean concentrations of either PCBs 118 or 180, thus fewer samples will contain PCB 33 below the SSDL.

The sensitivity for *trans*-nonachlor was similar to that for PCB 180, with 66% of the dissolved results below the SSDL and 41% of the particulate results below the SSDL.

4.3 Data Interpretation

4.3.1 Comparison to Historical Studies

There appear to be relatively few historical data on PCBs and *trans*-nonachlor available for the tributaries in the LMMB Study. Much of the published data focuses on the open lake, not the tributaries. Data for the Fox River are available from the Wisconsin Department of Natural Resources (DNR) based on their efforts to remediate PCB contamination in 39 miles of the lower Fox River emptying into Green Bay.

Those data are a combination of data collected in 1989 and 1990 and the data collected in the Fox River as part of the LMMB Study in 1994 and 1995. The results are for total PCBs, without any fractionation between dissolved and particulate phases. The individual results from each sample collected in 1989 and 1990 are not available in the DNR report, so no formal statistical comparisons could be made. The results are presented in a graph in the DNR report, in which the total PCB concentrations appear to range from near 0 to 120 ng/L in the 1989 - 1990 study, and from near 0 to 130 ng/L for the 1994 - 1996 data (collected as part of the LMMB Study). Moreover, DNR concluded that *"the Lower Fox River is the source of 95% of the PCB load to Green Bay and is the single largest tributary load to Lake Michigan."*

The data from the LMMB Study presented in Section 4.2 show that the mean concentrations of PCB congeners and total PCBs in the Fox River are among the highest of the 11 tributaries in this study. When combined with the flow data from the LMMB Study, these concentration data can be transformed into loads that can be compared to the loads from the other tributaries, and ultimately compared to the conclusions of the DNR report.

PCB data collected from large volume samples similar to those in the LMMB Study were reported from the Detroit River, which connects Lake Huron and Lake Erie (Froese *et al.* 1997). The samples were collected on eight occasions between March and October 1995 and on one occasion in May 1996. The investigators in that study reported that dissolved total PCB concentrations ranged from less than 5 ng/L to 13 ng/L, while particulate total PCB concentrations ranged from less than 5 ng/L to 22 ng/L, with a mean particulate concentration of 10 ng/L. Those results fall within the same general ranges as the dissolved and particulate results for the Fox, Grand Calumet, Kalamazoo, Milwaukee, and Sheboygan Rivers in this study, and are higher than the results for many of the other Lake Michigan tributaries.

Another earlier study addressed PCB concentrations in 14 major tributaries that discharge into Lake Michigan. Marti and Armstrong (1990) reported the results from between three and eight samples collected from each of the 14 tributaries from 1980 to 1983. The 14 tributaries in that study included 10 of the 11 tributaries in the LMMB Study (only the Grand Calumet River was not included). The sample volumes were approximately 16 liters, and were filtered and processed through a column of XAD-2® resin, in a fashion similar to that used in the LMMB Study.

As with the WDNR data, the results were reported for "total PCBs," however, in addition to the total PCB concentration (e.g., dissolved and particulate), Marti and Armstrong reported the percentage that represent the particulate PCBs. Where possible, they also assigned the PCBs to one of three Aroclors or Aroclor mixtures (1242 + 1248, 1254, and 1260).

For the 10 LMMB tributaries, Marti and Armstrong reported mean total PCB concentrations ranging from 9 to 103 ng/L, with the extreme values ranging from 4 to 262 ng/L in those 10 tributaries. Marti and Armstrong attributed from 53% to 83% of the "total PCB" concentrations to particulate-phase PCBs. In contrast, the sum of the mean dissolved and mean particulate total PCB concentrations in the LMMB Study ranged from 0.8 to 76 ng/L, while the percentage of the total PCBs attributable to the particulates ranges from 27% to 74%. Marti and Armstrong found the highest total PCB concentration in the Fox River (262 ng/L). The three highest mean concentrations were reported for the Sheboygan, Fox, and Milwaukee Rivers, at 103, 98, and 97 ng/L, respectively. The sums of the mean dissolved and particulate total PCB results from the LMMB Study for these same three tributaries are 81, 53, and 24 ng/L, suggesting that total PCB concentrations in these three tributaries decreased by 21% to 71% from 1980 to 1995.

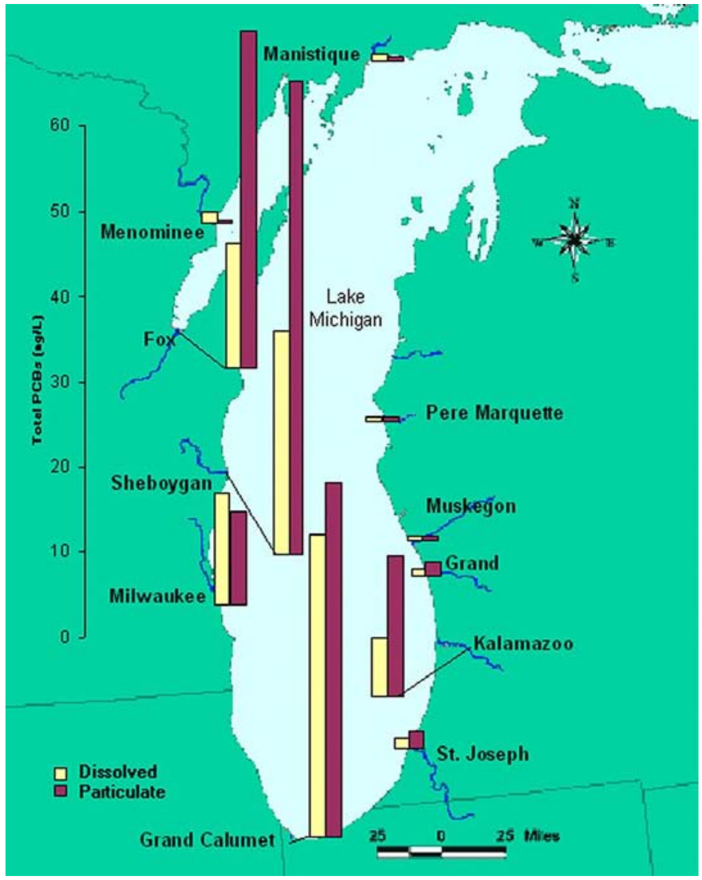
Data from the study also suggest that PCB concentrations are influenced by river flows as well as sediment PCB concentrations. Under low-flow conditions, total PCB concentrations in the Fox River were relatively high, possibly the result of the release of PCBs from sediments into the river water. As rivers flow increased, the total PCB concentrations decreased to the point of mean flow, and then increased again at higher flows. The total PCB concentration increase with increased flow is believed to be indicative of resuspension of PCB-contaminated sediments.

Marti and Armstrong also reported the results for 20 blanks processed through the filtration and extraction procedures applied to the tributary samples. The mean PCB concentration in the XAD-2 resin blanks was 1.1 ng/L ± 1.4 ng/L. The mean total PCB concentration for the filter blanks was 0.81 ng/L ± 0.76 ng/L. Therefore, although the Marti and Armstrong data from 1980-1983 suggest that there may have been significant decreases in PCB concentrations by the time of the LMMB Study, the results for the blanks in the Marti and Armstrong data are as large or larger than the LMMB Study total PCB results for at least five of the LMMB tributaries, complicating the evaluation of any historical trends, especially for the less polluted tributaries.

4.3.2 Regional Considerations

The results from this study generally support the assumptions used to design the study – namely that there are several tributaries that contribute large amounts of PCBs and *trans*-nonachlor to Lake Michigan and that there are other tributaries that have much lower concentrations (Figure 4-11). The tributaries that contribute the largest amounts of PCBs and *trans*-nonachlor are those near the Chicago metropolitan area and on the western shore of Lake Michigan (e.g., Grand Calumet, Milwaukee, Sheboygan, and Fox).

Figure 4-11. Mean Dissolved and Particulate Total PCB Concentrations in Lake Michigan Tributaries



As these results are converted into pollutant loads to the lake, management decisions can focus on those tributaries where reductions are most practical and on those that will have the greatest impact on the overall concentrations of contaminants in Lake Michigan.

4.3.3 Other Interpretations and Perspectives

In the Wisconsin DNR study of the lower Fox River described in Section 4.3.1, the investigators noted a correlation between the concentrations of chlorophyll *a* and particulate PCBs in the Fox River. That relationship was subsequently investigated in the Milwaukee and Manitowoc rivers with similar results (Fitzgerald and Steuer, 1996).

The possible relationship between particulate PCB concentrations and chlorophyll *a* was examined using the LMMB Study data. The particulate PCB results for 39 samples from the Fox River demonstrate a strong correlation with chlorophyll *a* for both individual PCB congeners and total PCBs, while the correlations in the Milwaukee River are not as strong (Table 4-11).

Table 4-11. Correlation of Particulate PCB and *trans*-Nonachlor Concentrations with Chlorophyll *a* in the Fox and Milwaukee Rivers

Particulate-Phase Analyte	Correlation with Chlorophyll *a* (r)	
	Fox River (n=39)	Milwaukee River (n=37)
PCB 33	0.845	0.343
PCB 118	0.901	0.625
PCB 180	0.884	0.595
Total PCBs	0.873	0.627
trans-Nonachlor	0.642	0.596

Fitzgerald and Steuer attribute the correlation to a combination of the low solubility of PCBs, and thus their affinity for particle surfaces, and active uptake of PCBs by algal cells. As a result, they consider PCBs in the particulate phase to be subdivided into the abiotic fraction, comprised of the PCBs associated with suspended particles including resuspended river sediments, and the biotic fraction, comprised of algae that have incorporated PCBs into their cells. This biotic fraction is the lowest link in the incorporation of PCBs into the food web.

Given the differences observed between the Fox and Milwaukee Rivers in Table 4-11, the correlations between particulate total PCBs and chlorophyll *a* were examined for all 11 tributaries in the LMMB Study (Table 4-12). The r-values for the correlations range from −0.180 to 0.895, with the strongest correlations in the Sheboygan, Kalamazoo, and Fox Rivers. The correlations do not appear to be related to overall particulate PCB concentrations because some relatively clean rivers have high correlations (e.g., St. Joseph), while some rivers with much higher PCB concentrations show very low or even negative correlations (e.g., Grand Calumet and Muskegon).

Data were collected for "total solids" during the LMMB Study. Total solids include both the suspended solids and the dissolved solids and therefore, the total solids results will overestimate the concentration of solid particles in the sample. However, there are strongly positive correlations between particulate total PCBs and total solids in many of the tributaries (Table 4-12). The correlations with total solids generally are similar to the correlations with chlorophyll *a* in most of the tributaries. The exceptions are the Grand Calumet and Muskegon Rivers. The correlation with total solids is very strong in the Grand Calumet River, while the correlation with chlorophyll *a* is very low. This suggests that the particulate PCBs in this tributary are almost exclusively "abiotic." In the Muskegon, both correlations are very low, and with different signs.

Table 4-12. Correlation of Particulate Total PCB Concentrations with Chlorophyll *a* and Total Solids in Lake Michigan Tributaries

Tributary	Correlation with Particulate Total PCBs (r)	
	Chlorophyll *a*	Total Solids
Fox River	0.873	0.848
Grand Calumet	0.094	0.841
Grand River	0.619	0.892
Kalamazoo	0.877	0.849
Manistique	0.443	0.354
Menominee	0.274	0.495
Milwaukee	0.627	0.826
Muskegon	-0.180	0.056
Pere Marquette	0.613	0.591
Sheboygan	0.895	0.859
St. Joseph	0.718	0.786